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Obtaining higher fatty alcohols based on low molecular polyethylene and their useage as lubricating additives for diesel fuels

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ABSTRACT

One of the ways to change the physicochemical properties of diesel fuels is to add so-called additives to it. The purpose of this work is to obtain higher fatty alcohols and the use of qualitatively new imported - substituted additives, synthesized on the basis of the use of local secondary raw materials, which is increases their efficiency.

Key words: polyethylene, oxosynthesis, refining, hydrogenation, fatty acids, catalyst.

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I.Introduction

Since Uzbekistan gained independence and the beginning of economic reforms in the republic, special attention is paid to the oil and gas complex. Since that time, a new stage began in the development of the oil and gas industry. Today, the modernization and reconstruction of the Bukhara oil refinery is aimed at improving the quality of oil products from Euro-2 requirements to the requirements of the Euro-5 environmental standard and at increasing the depth of processing of raw materials from 79% to 95%. After modernization, when the total amount of sulfur in the composition of the produced diesel fuel is reduced from 500 ppm to 10 ppm, then its lubricating properties sharply decrease, which is scientifically based on world experience. Consequently, one of the urgent problems today is the production of import-substituting multifunctional additives for diesel fuel based on local secondary raw materials, which improves its lubricating properties.

On the basis of higher fatty alcohols, various additives for fuels and lubricants are produced. These include polymeric esters of methacrylic, di-thiophosphoric and other organic and inorganic acids [1-3].

Esters of C7-C9 alcohols and methacrylic acid serve as the basis for the production of viscous and depressant additives for motor fuels and oils. One of the types of thickening additives are polymerizates of esters of methacrylic acid and monohydric alcohols (molecular weight of polymers is from 5000 to 20,000). The best indicators are given by octyl alcohol-based polymethacrylates added to oils in an amount of 2 to 6%.

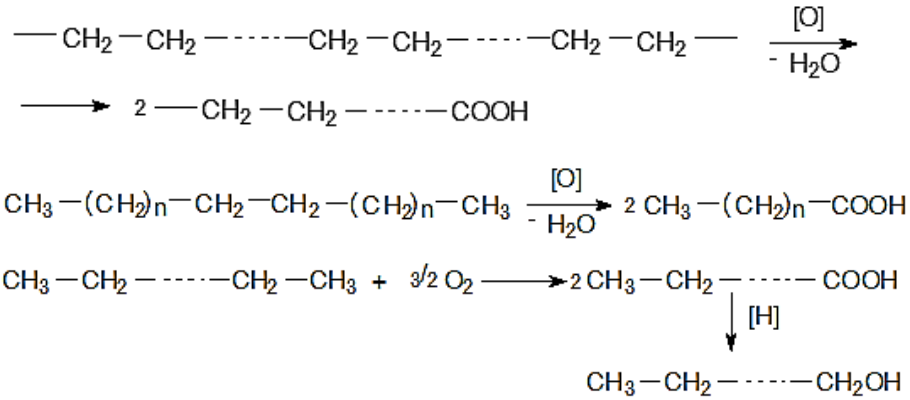
It is known that higher fatty alcohols are synthesized in different ways based on petrochemical raw materials and by the method of reducing carboxylic acids isolated from natural fats.

For the production of higher fatty alcohols, dozens of methods are used, which include: direct hydrogenation of synthetic fatty acids; hydrogenation of synthetic fatty acid methyl esters; hydrogenation of natural fats; hydrogenation of paraffin oxidation products; direct oxidation of paraffin to secondary alcohols; the separation of alcohols from the second unsaponifiable production of synthetic fatty acids of organoaluminum synthesis and oxosynthesis.

We obtained fatty alcohols by hydrogenation of paraffin oxidation products, as well as low molecular weight polyethylene (LMPE) as follows: NMPE and paraffins were oxidized with air oxygen, the oxidized paraffin was washed, then the oxidant was hydrogenated on a zinc-chromium catalyst, the hydrogenate was separated into two fractions, the first fraction of the hydrogenate was esterified with boric acid, then hydrocarbons were distilled off from borates, washed and returned to hydrolysis, borates were regenerated, the alcohols were hydrotreated on copper-chromium catalysts, then the alcohols were rectified into 5 fractions. The yield of primary alcohols reached 97-99%.

As well as in laboratory conditions, synthetic fatty acids were obtained using catalysts by oxidation of oil waste with low molecular weight polyethylene at 100–1060C with oxygen. Fatty alcohols were then obtained by hydrogenation. This process proceeded according to the indicated scheme:

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Since, during oxidation, the breakdown of the paraffin molecule occurs in different places, the result is a mixture of fatty acids with different numbers of carbon atoms. Then the mixture was distilled on a reflux column to isolate a narrow fraction. To prepare additives that improve the quality of diesel fuel, we used two fractions C10 – C16 and C17 – C20, respectively.

The initial fraction is similar in its characteristics to acids obtained from paraffin. The composition and properties of the first and second fractions are discussed in tables 1 and 2.

Table 1

The approximate composition of the I fraction C10-C16

Fractions	FA content,% mass
До C_{10}	4,5–6,4
C_{10}–C_{11}	22,0–26,5
C_{12}–C_{13}	47,3–48,6
C_{14}–C_{16}	30,2–34,0
above C_{16}	17,6–21,5

Table 2

Approximate composition of II fraction C17-C20

Фракции	FA content,% mass
Up to C_{17}	26,4–41,3
C_{17}–C_{18}	22,2–24,1
C_{17}–C_{20}	43,5–49,2
above C_{20}	13,9–24,7

If acids with fewer carbon atoms in the chain get into the fraction of fatty acids C10 – C16, then their properties decrease, and the solubility and consumption in water itself increases. This increases the consumption of fatty acids.

Impurities in the second C17 – C20 fraction of fatty acids with more than C20 carbon atoms are also not at all desirable. Since it becomes necessary to increase the temperature, slow down the solubility of the substance.

In the fractionation of synthetic fatty acids into fractions, a small amount of non-saponifiable paraffinic hydrocarbons is simultaneously distilled off as side components. The physical and chemical characteristics of synthetic acids are shown in table. 3.

Table 3

Properties of synthetic fatty acids

Indicators	Fraction of fatty acids	
	C_{10}–C_{16}	C_{17}–C_{20}
Acid number, mg potassium hydroxide / g, no more than	241,3–264,2	188,1–210,4
Saponification number, mg potassium hydroxide / g, no more than	250,5–270,2	195,7–218,3
Iodine number, mg iodine / 100 g, no more than	7,3–10,5	15,6–18,4
Content of non-saponifiable substances,% wt., No more	2,2–3,6	5,7–6,9
The content of iso-acids,% wt.	1,5-4,7	21,8–26,9
Pour point, ^{0}C	31,3–32,5	43,7–51,5

If fatty acids of traces of Fe get into the considered fractions, then even during storage and transportation they begin to darken and acquire a specific smell. [4.5].

With the improvement of the oxidation processes of paraffinic hydrocarbons and with ensuring the purity of the extracted components from undesirable compounds, the amount of synthetic fatty acids in the composition of the obtained substance will increase, up to a composition using 100% synthetic raw materials. Fatty acids of the C17 – C20 fraction are often used instead of solid fats; fraction C10 – C16 - instead of coconut oil. This fraction is close to liquid

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oils in terms of its effect on titer, due to the presence of branched acids in its composition.
Primary fatty alcohols based on the hydrogenation of the products of paraffin oxidation are also characterized by high quality. These alcohols are represented by 97% primary alcohols, of which 90-92% have a linear structure.
Hydrogenation products were identified by IR and NMR spectroscopy, as well as by chromatographic analysis. We analyzed the composition of the reaction products by GLC on a Hewlett Packard 6890 chromatograph with a thermal conductivity detector. Separation of the components of the reaction mixture was carried out on an HP-InoWax column with a stationary phase of polyethylene glycol deposited in the temperature programming mode (5 ° C / min) from 50 ° C (5 min) to 220 ° C.

Evaporator and detector temperature 200 ° C, helium carrier gas. We processed the chromatogram data using the Chemstation program.
The IR spectrum was recorded on a SPECORD spectrometer. The NMR spectrum was recorded on a Gemini-200 spectrometer from Varian, with an operating frequency for 1H nuclei of 200 MHz and for 13C nuclei 50 MHz at 34.5 ° C with an external or internal standard TMS in CdC13 or CdCl4 ...

The assignment of signals in the 13C and 1H spectra was carried out by comparing with the spectra of the initial components, by calculating by additive schemes, and also by comparing with the literature data [6]. Assignment of signals in the 1H NMR spectrum: -CH2OH – 3.6 ppm, OH - 3 ppm, -CH2CH2OH – 1.52 ppm, –CH2 - 1.2 ppm, –CH3– 0.85 ppm, 13C NMR spectrum: CH2OH– 62.8 ppm, –CH2CH2OH– 32.8 ppm, –CH2 - 22-30 ppm, –CH3– 14.1 ppm.
To eliminate the inaccuracies inherent in the method for extracting primary alcohols by hydrogenating methyl esters of synthetic fatty acids, copper-chromium and copper-chromium catalysts were used. The most important stages of the technological process for the manufacture of original fatty alcohols: reduction of synthetic fatty acids to alcohols by direct hydrogenation, saponification of "raw" alcohols, drying and fractionation of the acquired fatty alcohols.
The process of extracting fatty alcohols is distinguished by the refining of the acquired esters, and also there is no stage of esterification of acids, the simplicity of the units for manufacturing and dosing the catalyst suspension, this eliminates the need to use methanol, and sulfate-containing industrial waters are not formed.
It can also be observed that some disadvantages were discovered when the hydrogenation took place. For example, during hydrogenation, due to the reduced mechanical strength of the catalyst, it begins to deteriorate, and this leads to plugging of apparatus, erosion of pipes and equipment. As a result of the reduced space velocity during hydrogenation (0.13-0.21 l / h), a large amount of hydrocarbons (5.0-11.0%) was found in the resulting product. This technique can get rid of the above disadvantages in the process of direct hydrogenation of complex fatty acids on suspended copper-chromium-barium catalysts.

The volumetric rate of the hydrogenation of complex fatty acids on a suspended catalyst increases many times more, in contrast to the direct reduction of complex fatty acids on a stationary copper-chromium catalyst.
Gas-phase hydrogenation is demanding on the evaporation of the substrate and because of this, a part is used for esters of synthetic fatty acids with a chain length of 12-14 carbon atoms. Zinc copper or chromium copper catalysts were used in a fixed bed. Optimal conditions: less than 10 MPa and a temperature of 240-255 ° C. Received fatty alcohol 98-99%.
An effective method for the synthesis of alcohols due to the use of a copper-chromium-barium catalyst at the stage of the hydrogenation process has certain advantages: a high conversion of fatty acids (98-99%) at the esterification stage, an increased rate of production of primary fatty alcohols at a 98% conversion of the initial feedstock, and a minimum growth of hydrocarbons [7,8].

The synthesis of higher fatty alcohols based on the use of local secondary raw materials, the addition of which improves the lubricating and viscous properties of diesel fuel, is currently considered a hot topic. Based on this, the priority task is to obtain such alcohols that can be used as additives for diesel fuels. Thus, the introduction of additives obtained by us from higher fatty alcohols into diesel fuel leads to an improvement in the physicochemical properties.

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